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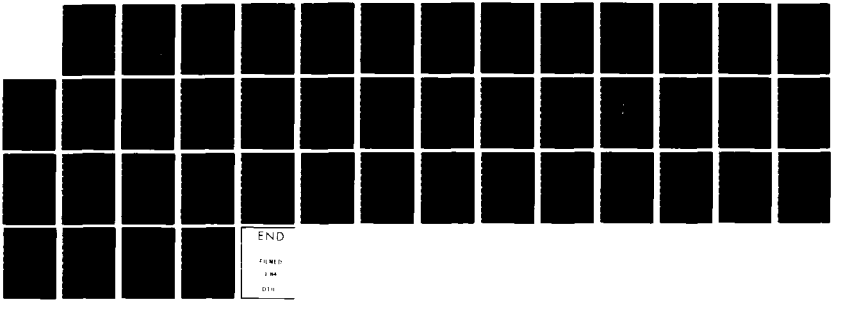

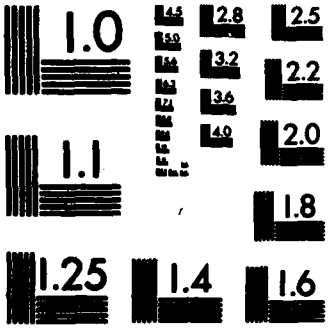

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STUDIES OF SILICON REFRACTORY METAL INTERFACES: PHOTOEMISSION STUDY OF INTERFACE FORMATION AND COMPOUND NUCLEATION

FINAL REPORT

JOHN H. WEAVER

9/12/83

U.S. ARMY RESEARCH OFFICE

DAAG29-81-K-0140

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- A Franciosi, D.J. Peterman, J.H. Weaver, and V.L. Moruzzi, "Structural Morphology and Electronic Properties of the Si-Cr Interface," Phys. Rev. B 25, 4981-4993 (1982).
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Invited Paper at APS National Meeting on Metal-Silicon Interfaces and Silicides

Papers at two Conferences on Physics and Chemistry of Semiconductor Interfaces

Seminars at IBM Yorktown Heights, University of Pittsburgh, University of Minnesota

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We have examined the electronic and morphological interactions which occur at the interface between silicon and a variety of metals, including Cr, Ti, Sm, Au, and Ca. These interface studies were supported by extensive synchrotron radiation photoemission studies of bulk silicides, including Ti_2Si_5, $TiSi_2$, $NbSi_2$, VSi_2, $CrSi_2$, $MoSi_2$, $TaSi_2$, $FeSi_2$, $CoSi_2$, Ni_2Si, NiSi, $NiSi_2$, and Pd_2Si and by calculations of the density of states of silicides (Moruzzi at IBM; Bisi and Calandra at Modena). We have sought to identify the important parameters in the formation of the metal-silicon bond. We have demonstrated the systematic development of the Si-metal p-d hybridization and the reduction of the Si sp^3 bond.

Major breakthroughts include:

1. The discovery of the commonality of the Si-metal p-d bond in the transition metal silicides, a bond which is responsible for stability of silicides and reflects selective hybridization of metal and silicon states. These bonds are basically the same in all metal silicides and their evolution is reflected in the formation of interface silicides. Understanding the details will be the key to understanding the interface itself.

2. The discovery that the formation of interfaces proceeds in three basic stages, namely the chemisorption stage where the adatom is relatively weakly bound to the surface, the reactive stage where chemical reaction and interdiffusion occurs, and the covering-up stage where the overlayer of metal is basically metal-like in character but contains outdiffused Si nonetheless.

3. The discovery that Si outdiffusion can be controlled by thin interlayers between Si and a metal overlayer. By examining the Si-Cr-Au junction, we found clear evidence that control can be accomplished by changing the character of the interlayer, i.e. if the interlayer is fully reacted it will enhance outdiffusion whereas if it is in the chemisorption or covering-up regime it will act as a barrier. This was the first time that such catalytic effects were observed and were correlated to the chemical character of the interlayer.

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Author: John H. Weaver

Manuscripts submitted and published:

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Invited Paper at APS National Meeting on Metal-Silicon Interfaces and Silicides

Papers at two Conferences on Physics and Chemistry of Semiconductor Interfaces.

Seminars at IBM Yorktown Heights, University of Pittsburgh, University of Minnesota

Personnel: John H. Weaver - Principal Investigator
Alfonso Franciosi - Postdoctoral Associate
David G. O'Neill - Ph.D. Student

Brief Outline of Research Findings:

We have examined the electronic and morphological interactions which occur at the interface between silicon and a variety of metals, including Cr, Ti, Sm, Au, and Ca. These interface studies were supported by extensive synchrotron radiation photoemission studies of bulk silicides, including Ti_5Si_3, $TiSi_2$, VSi_2, $NbSi_2$, $CrSi_2$, $MoSi_2$, $TaSi_2$, $FeSi_2$, $CoSi_2$, Ni_2Si, NiSi, $NiSi_2$, and Pd_2Si and by calculations of the density of states of silicides, (Moruzzi at IBM; Bisi and Calandra at Modena). We have sought to identify the important parameters in the formation of the metal-silicon bond. We have demonstrated the systematic development of the Si-metal p-d hybridization and the reduction of the Si sp^3 bond.

Major breakthroughs include:

1. The discovery of the commonality of the Si-metal p-d bond in the transition metal silicides, a bond which is responsible for stability of silicides and reflects selective hybridization of metal and silicon states. These bonds are basically the same in all metal silicides and their evolution is reflected in the formation of interface silicides. Understanding the details will be the key to understanding the interface itself..

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3. The discovery that Si outdiffusion can be controlled by thin interlayers between Si and a metal overlayer. By examining the Si-Cr-Au junction, we found clear evidence that control can be accomplished by changing the character of the interlayer, i.e. if the interlayer is fully reacted it will enhance outdiffusion whereas if it is in the chemisorption or covering-up regime it will act as a barrier. This was the first time that such catalytic effects were observed and were correlated to the chemical character of the interlayer.

Silicon–refractory metal interfaces: Evidence of room-temperature intermixing for Si–Cr

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(Received 17 February 1981; accepted 11 May 1981)

Photoemission spectroscopy investigations of the Si–Cr interface using synchrotron radiation indicate metal–semiconductor intermixing during room temperature interface formation, in sharp contrast with the Si–V interface. The intermixed phase is 10–13 Å thick and is of definite metallic character. For higher metal coverage (≳20 monolayers) photoemission from Si 2*p* levels with variable surface sensitivity show Si segregation in the top layers of the Cr film.

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In this communication we report the first photoemission study of a silicon–refractory metal interface in which the tunability of a synchrotron light source has been exploited to examine valence band and core level emission features. Valence band emission from the interface region shows dramatic modifications of the Cr-derived 3*d* density of states as a function of metal coverage and suggests the formation of an *intermixed* interface. The intermixed phase, formed at room temperature, shows a definite metallic character while $CrSi_2$, the only bulk chromium silicide known to form upon heat treatment (at 450°C) of evaporated Cr on Si, was reported to be a semiconductor.[1] Emission from the Si 2*p* core levels confirms the intermixing and suggests an escape depth-driven exponential attenuation of the Si-derived emission from the interface region at higher metal coverages (12–20 monolayers). Deviations from the exponential behavior are shown at higher coverages and, correspondingly, Si-core photoemission indicates Si segregation at the surface of the metal film.

An increasing amount of experimental and theoretical information is becoming available on Si–noble metals and Si–near-noble metal systems,[2–5] but much less is known about the formation of Si–refractory metal junctions. The silicon–refractory metals systems are interesting from a technological point of view. Refractory metal silicide growth by heat treatment of the interface[6] is a most promising way of obtaining metallization patterns and new gate materials for very large scale integrated circuits.[7] This process may also be valuable for obtaining conductive layers stable at high temperature for high concentration solar cell systems[8] or solid state thermoelectric generators.[9] We have started systematic investigations of the electronic properties of bulk Si–refractory metal compounds[10] and here we present our first results on interface formation. We hope in this way to contribute to a better understanding of the chemical bonding and structure of metal–semiconductor interfaces.[11,12]

In this paper we present photoemission spectroscopy studies with synchrotron radiation of the Si(111)–Cr interface. Si(111) substrates were obtained by cleaving *n*-type, phosphorous-doped (1.5 Ω cm) Si single crystals in an ultrahigh vacuum system (operating pressure $\lesssim 4 \times 10^{-11}$ Torr (5.3×10^{-9} Pa)). The experimental setup has been described elsewhere.[13] Substrate cleanliness was monitored by detecting the Si(111) 2×1 surface state emission.[14] Cr films (99.99% pure) were prepared by sublimation of Cr from a Ta boat using liquid nitrogen cooled electrodes [pressure $\lesssim 2 \times 10^{-10}$ Torr (2.6×10^{-8} Pa) during evaporation]. We emphasize that the high reactivity of the refractory metals imposes severe restrictions on the operating pressure. The high temperature intermixing process itself is very sensitive to the presence of contaminants[6] for the Si–refractory metal interfaces. The coverage, θ, was monitored with a quartz thickness monitor and is given in terms of Si(111) surface atomic density (θ = 1 monolayer at $\sim 7.6 \times 10^{14}$ atoms/cm^2). Synchrotron radiation from the 240 MeV electron storage ring Tantalus was monochromatized with a toroidal grating monochromator in the photon energy range of 10–135 eV or with a Seya–Namioka type monochromator ($10 \lesssim h\nu \lesssim 30$ eV). The photoelectrons were energy analyzed by a double pass cylindrical mirror analyzer.

Studies of the Si–Cr interface were carried out at ~300 K (RT) for metal coverages of 0.1 to 50 monolayers. In this paper we report the interface behavior for $\theta \gtrsim 1$. For submonolayer coverages we mention here[14] that the emission from the Si(111) intrinsic surface states is dramatically reduced at the lowest coverages ($0.1 \lesssim \theta \lesssim 0.4$) without any detectable change of the Fermi level pinning position.[15]

In Fig. 1 we show photoelectron energy distribution curves (EDC's) for a photon energy of 21 eV to reveal the effects of Cr deposition. The bottommost EDC for a clean Si(111) surface shows the well known Si valence band features and the intrinsic surface state emission. Successive EDC's displayed upward correspond to increasing Cr coverage and are normalized to the incident photon flux. The uppermost curve shows the emission spectrum of a thick Cr film (~300 Å) evaporated onto oxidized tantalum and is in good agreement with the data for bulk samples.[16] The emission spectrum for a given coverage was found to be independent of the way the interface was obtained, i.e., if with one evaporation or with a series of depositions. As shown in Fig. 1, at $h\nu = 21$ eV the emission features of the Si substrate are visible up to coverages of 2–3 monolayers. For higher coverages no substrate emission features are visible, as shown by the complete disappearance of the Si bulk feature ~7.5 eV below E_F.

For $\theta \gtrsim 2$ Fig. 1 clearly shows that the valence band is dominated by Cr-derived 3*d* emission, although for coverages

of the band structure of the intermixed Cr–Si phase is beyond the scope of this paper, we note that the intermixed phase has a definite metallic character, as shown by the high density of states at E_F in Figs. 1 and 2. Since resistivity measurements have shown that $CrSi_2$ is a semiconductor with a 0.35 eV band gap,[1] it is clear that room temperature intermixing gives rise to a phase with electronic structure strikingly different from $CrSi_2$. For the Si–V interface, Claber and Rubloff[17] reported the formation at 350°C of an intermixed phase with an overall V/Si ratio of ~1 while the only known interface compound is VSi_2 which forms at 500°C.[6] In this connection, we are starting more systematic studies to determine whether or not strongly intermixed phases are generally formed before silicide nucleation at Si–refractory metal interfaces. This would be a totally new notion of the behavior of these interfaces.

Room temperature intermixing is somewhat more surprising for silicon-refractory metal than for the other silicon–transition metal interfaces. Silicon–refractory metal interfaces show much higher activation energies and formation temperatures for compound (disilicide) growth.[6] Two very different models for silicon–silicon bond breaking have been proposed in the two cases.[21] For the refractory metal silicides the high formation temperature (typically 600°C) was related[21] to a phonon assisted mechanism of silicon–silicon bond breaking.[6,21] The room temperature intermixing for the Si–Cr system and the formation of an intermixed phase at 350°C for Si–V suggest that the microscopic situation at the interface is more complicated than expected.

Room temperature and liquid nitrogen temperature intermixing at silicon–metal interfaces has been associated with the condensation energy of the metal onto the semiconductor surface.[22] The different behavior of Si–Cr with respect to Si–V would imply that this energy contribution is sufficient to promote the intermixing only in the case of Cr. In this respect we note that within all Si–refractory metal interfaces the Si–Cr system[6] has the lowest formation temperature (450°C) and the lowest activation energy (1.7 eV) for bulk compound growth ($CrSi_2$). Further investigations are strongly needed, including temperature dependent studies of the formation of Si–refractory metal interfaces and of the Si–Cr one in particular.

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Structural morphology and electronic properties of the Si-Cr interface

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(Received 16 November 1981)

Photoemission studies ($12 \lesssim h\nu \lesssim 135$ eV) of room-temperature formation of the Si-Cr interface show reactive behavior with atomic intermixing and dramatic modifications of the metal-derived d density of states. Self-consistent augmented-spherical-wave calculations of the total and l-projected densities of states for the silicides Cr_3Si, CrSi, and $CrSi_2$ in simplified cubic lattice structures allow an identification of general trends in the electronic structure upon Si-Cr heteropolar bond formation. These experimental and theoretical results suggest an interface morphology where a Si-rich intermixed phase is present for a depth of $\simeq 10$ monolayers between the Si crystal and the unreacted Cr film. Evidence of Si segregation in the top layers of the Cr film is provided.

I. INTRODUCTION

Silicon-metal junctions have a well-known importance in modern electronics technology and a large number of experimental and theoretical efforts have been devoted to defining the basic mechanisms which determine their electronic and structural properties.[1–6] These diverse efforts are revealing fascinating physical and chemical properties of interfaces, properties which have important ramifications in the fundamental understanding of interfacial phenomena and in the technological use of semiconductor devices.[7,8]

Si-refractory metal interfaces are extremely interesting systems in connection with very large scale integrated-circuit technology,[8] but their microscopic structural and electronic properties have received very little attention. In this paper we deal with the mechanisms driving Si-Cr interface formation.

We have conducted valence-band and core-level photoemission studies with synchrotron radiation as a function of metal deposition on the Si(111)-(2×1) surface. We have also performed calculations of the electronic structure for a series of Si-Cr model compounds to gain insight into the modification of the electronic states due to Si-Cr heteropolar bond formation.

Among the important conclusions of the present study are the following.

(1) The intrinsic Si surface-state emission is dramatically reduced at submonolayer Cr coverage but there is no detectable change of the Fermi-level pinning position.

(2) At room temperature, an intermixed phase of metallic character is formed at the silicon-chromium interface and comparison of experimental and theoretical results suggests that this intermixed phase is Si-rich.

(3) The valence-band emission and measured Schottky barrier height of this interface differ from what is expected for a Si-$CrSi_2$ interface.

The implication is that the Si-Cr interface may not follow trends observed for other Si-metal interfaces. In other reactive interfaces, the intermixed phases formed at room temperature have electronic structures similar to those of the "bulk" silicides grown by high-temperature film reaction.[1,4,5] In Si-Cr, the intermixed phase is metallic whereas the bulk silicide $CrSi_2$ is expected to be a small-gap semiconductor. Si-refractory metal interfaces show, in fact, remarkably different properties for compound growth (stoichiometry and kinetics)[8,9] from other Si-metal interfaces. For the Si—near-noble-metal interfaces, for example, moderate annealing (250 °C) results in growth of Ni_2Si, Pd_2Si,

one set of parameters that gives reasonable agreement between theory and experiment for both $h\nu = 120$ and 135 eV. In Fig. 8(d) the best agreement is obtained for a concentration n_c of 1.17×10^{12} islands/cm^2, with an island radius of ~ 22 Å at $\Theta = 3$, while in Fig. 8(e) we obtained some agreement choosing $n_c = 4.10 \times 10^{10}$ islands/cm^2, with islands of ~ 68-Å radius at $\Theta = 3$. The fact is that in assuming a Volmer-Weber growth of an unreacted Cr film, the escape depth difference ($L = 5-7$ Å for $h\nu = 135$ eV and $L = 10-12$ Å for $h\nu = 120$ eV) is not enough to explain the strong difference in the attenuation rate of the experimental spectra in Figs. 8(d) and 8(e). Such a difference can be accounted for by assuming that reaction does occur at the interface and that an extended intermixed region forms upon Cr deposition on the Si surface.

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[29]In the present case the only available Cr core level was the shallow 3*p* with overall photoemission intensity that made it unsuitable for coverage-dependent studies. Even in those cases where it is possible to monitor core binding energy shifts of both elements upon binary compound formation, the observed "chemical shift" need not be related in an elementary way to the actual charge transfer: see, for instance, R. E. Watson and M. L. Perlman, Struct. Bonding 24, 82 (1975). Charge transfer in energy band calculations is difficult to define because it depends on the manner in which space is allocated to the different constituents. As a further complication, we vary the lattice constant of the compound (by systematically changing the sphere volumes of the constituents) in order to determine the minimum total energy (theoretical equilibrium). In our calculations, the space allocation of the constituents is determined by calculated bulk modulii and volumes of the constituents in their elemental forms. In changing the volume of the compound (to find theoretical equilibrium), a constituent with a large elemental volume and a small elemental bulk modulus suffers a larger volume change than one with a small elemental volume and a large elemental bulk modulus. The charge transfers referred to in this work are all based on this construction.

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Electronic structure of nickel silicides Ni_2Si, NiSi, and $NiSi_2$

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Synchrotron-radiation photoemission studies of bulk samples of Ni_2Si, NiSi, and $NiSi_2$ show valence-band emission dominated by Ni $3d$—derived features. These d bands shift toward E_F and broaden with increasing Ni concentration and Ni-Ni interaction, falling at -3.2 eV for $NiSi_2$ and -1.3 eV for Ni_2Si. In each case, the density of states near E_F is very low. These results are interpreted in terms of recent calculations which are shown to forecast correctly the general trends and modifications of the silicide electronic structure. Further, they indicate that the d-band features observed in photoemission reflect d states which are not directly involved in the Ni—Si bonds. Core-level studies show that charge transfer plays a minor role in the chemical bond, but changes in the electronic configuration account for the observed shifts in the Ni $3p$ binding energy.

The structural and electronic properties of metal silicides are receiving increasing attention in connection with efforts to understand the behavior of reactive Si-metal interfaces.[1] Most transition metals and near-noble-metals can react with silicon at low temperatures or even at room temperature to form thin silicidelike phases.[2–7] The presence of such reaction products at the interface determines the properties of electronic devices and is of paramount importance in the new technology of very large scale integrated circuits.[8]

To better understand chemical bonding at the interface and to identify potential structural and electronic differences between bulk silicides and these silicidelike phases, one must examine both bulk and interface silicides. However, very little is known about the electronic structure of bulk silicides.[9] In this paper we discuss a photoemission investigation of the bulk nickel silicides Ni_2Si, NiSi, and $NiSi_2$. These results have direct bearing on interface studies and they are also important from the point of view of bulk electronic structures of alloys because one rarely has an opportunity to study several stable phases of an alloy and observe systematics in the electronic structure.

The measurements discussed here reveal well-defined trends in the electronic structure of the silicide series and allow us to make comparison with a number of recent density of states calculations. The Ni $3d$—derived band is shown to dominate the valence-band spectra and to vary substantially in binding energy and width when going from Ni_2Si to $NiSi_2$. This trend reflects the reduced d-d hybridization in the Si-rich silicides. Core-level photoemission results show that ionicity plays a minor role in the silicide chemical bond; configuration and possibly relaxation effects explain the observed shifts in binding energies.

EXPERIMENTAL

The samples were prepared by comelting high-purity nickel and silicon in a nonconsumable arc furnace. The melts were made on a water-cooled copper hearth under a purified argon atmosphere. Ni_2Si and NiSi melt congruently and formed relatively large grains; $NiSi_2$ forms peritectically at 980°C. To ensure that the peritectic reaction was completed, and to enhance grain growth, the $NiSi_2$ casting was heated for five days at 950°C. Metallographic examination showed the samples to be single phase and analysis verified that they were stoichiometric.

All measurements were performed in an ultrahigh-vacuum photoelectron spectrometer (operating pressure $\lesssim 4\times10^{-11}$ Torr). Clean surfaces were obtained by fracturing the samples *in situ* and then moving them to the common focus of the monochromatic synchrotron radiation beam and the electron energy analyzer. Details of the experimental system have been given in Ref. 10.

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[18]The effect is actually larger since lifetime broadening increases in $NiSi_2$ because the 3*d* hole is deeper in energy with respect to E_F. Two different mechanisms can describe this band narrowing, i.e., the Heine inverse fifth power effect (Ref. 19) which is due only to the increase in atomic separation, and the reduced 3*d* tunneling effect (Ref. 20) in alloys with *sp* elements. The rate at which 3*d* electrons of a given energy tunnel through the $l(l+1)/r^2$ centrifugal barrier from a given site to a nearest-neighbor site is proportional to the density of final states at that energy associated with the nearest-neighbor site (Ref. 19). When Ni nearest neighbors are replaced by silicon atoms, the much lower density of final states leads to narrower *d* bands.

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Chemical bonding at the Si–metal interface: Si–Ni and Si–Cr

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Chemical bonding at the interface of a near-noble-metal (Ni) and a transition metal (Cr) with Si is examined through synchrotron radiation photoelectron spectroscopy studies of *in situ* formed interfaces, of cleaved bulk silicides, and of disordered surfaces prepared by sputter etching of the silicides. Interpretation of these experimental results is guided by parallel linear combination of atomic orbitals (LCAO) (extended Huckel approximation) calculations of stoichiometric Ni and Cr silicides.

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I. INTRODUCTION

For most silicon–metal systems, chemical reactions occur in the interface region even during room-temperature junction formation.[1] The characterization of the reaction products is of fundamental importance in understanding interface and Schottky barrier[2] formation and silicide growth.[3]

It was recently shown that room-temperature deposition of Ni, Pd, and Pt on Si gives rise to silicidelike reaction products at the interface.[1,4] Such phases have electronic structures close to, but not identical to, the metal-rich silicides Ni_2Si, Pd_2Si, and Pt_2Si. The differences have been ascribed to composition gradients in a smoothly varying interface region,[1,4] to local bonding distortions at an otherwise sharp interface between Si and an ordered, stoichiometric silicide,[5] and to the presence of interstitial metal atoms in the Si lattice neighboring the silicide–metal interface.[5] Less is known about Si–refractory metal interfaces but it has been suggested[3] that different mechanisms control silicide nucleation in these systems since they exhibit higher formation temperatures, different first nucleation phases (disilicides) and growth kinetics than do Si–near noble metal interfaces.

Many of the existing controversies and ambiguities in the interface literature reflect, in our opinion, an incomplete knowledge of the electronic structure of bulk stoichiometric silicides and the physical parameters which affect them. To address some of these interesting problems, we have performed photoemission studies with synchrotron radiation of *in situ* cleaved bulk samples of Ni_2Si, NiSi, $NiSi_2$,[6] and $CrSi_2$[7] and compared our data with calculations of the electronic density of the states for Ni_2Si, NiSi, $NiSi_2$, Cr_3Si, CrSi, and $CrSi_2$.[7,8] In addition, we have examined the electronic properties of Ar sputtered $NiSi_2$ so as to consider the effects of long-range order and of large deviations from stoichiometry. These results are compared with interface results.[9]

The photoemission experiments used radiation from the 240 MeV electron storage ring Tantalus. A toroidal grating monochromator was used to disperse the radiation. Photoemission and Auger measurements[10] were performed with a double-pass cylindrical mirror electron energy analyzer. Rutherford backscattering and channeling measurements helped characterize the samples used in the sputtering experiments of Si–Ni.[9] Total and *l*-projected density of states calculations were performed for stoichiometric silicides using the LCAO method in the extended Huckel approximation.[8]

II. Si–Ni

In Fig. 1 we compare photoemission spectra[6] for Ni_2Si, NiSi, and $NiSi_2$ taken at $h\nu = 50$ eV with the density of states calculated for the stoichiometric compounds. As shown, the calculations are in very good agreement with experiment. The valence bands are dominated by Ni 3*d*-derived features which shift toward E_F and broaden with increasing Ni concentration and Ni–Ni interaction. Comparison with theory shows that the valence band emission is most sensitive to Ni *d* states that are not directly coupled with Si-derived orbitals, i.e., nonbonding *d* states. The bonding Si-p/Ni-d states, shown shaded in Fig. 1, are relatively invisible since they are fewer in number and are more extended in energy than the nonbonding Ni-*d* states. The calculations and experiment show that the Ni-derived nonbonding states are modified as the Ni 3*d*–Ni 3*d* interaction changes in the silicide series. The main 3*d* feature (arrow, Fig. 1) falls 3.2 eV below E_F for $NiSi_2$, at 1.8 eV below for NiSi, and 1.3 eV below for Ni_2Si. The apparent full width at half maximum (FWHM) increases by more than a factor of two on going from the low-Ni compound $NiSi_2$ to the Ni-rich silicide Ni_2Si. At the same time, the binding energy of the Ni 3*p* core levels varies in a way which is nearly identical to that of the center of the *d* bands. In contrast to this, the binding energy of the Si 2*p* levels does not change appreciably[9] and therefore the effect of charge transfer is compensated by the change in relaxation and other potential changes in all cases and does not appear to be systematically related to the observed core shift.

again emphasize the nonbonding 3*d* features, as we found to be the case for the Ni–silicides (Fig. 1). The *d*-states that are predicted to be directly involved in the bonding with Si are relatively invisible in our data, presumably because the Cr–*d*/Si–*p* hybridization modifies the partial photoionization cross sections for these states.

As was the case for Ni silicides, the nonbonding *d*-states reflect the reduction of the Cr–Cr interaction which accompanies decreased metal content in the Cr silicide sequence. The calculations clearly indicate that the width of the nonbonding 3d manifold, which is determined primarily by 3*d*–3*d* interaction, decreases but they also show that these bands are cut by E_F. Since only the *d*-states below E_F are visible in photoemission, changes in composition are observed less dramatically in photoemission spectra for Si–Cr than for Si–Ni.

During room-temperature formation of the Si–Cr interface, photoemission spectra from valence and core levels indicate that Si–Cr intermixing occurs at the interface for metal coverage up to ~10 monolayers.[16] The 3*d* valence band emission for the intermixed phase is substantially different from that of bulk Cr: The main 3*d* emission feature shifts toward E_F with increasing metal coverage for $\theta < 10$ and then back toward its position in bulk Cr for $\theta > 10$. Correspondingly, a very small shift of the Si 2*p* cores to lower binding energy is observed. Comparison of our experimental and theoretical results for Cr silicides shows that these intermixed phases are Si-rich.

The valence band spectra for the interface region with $\theta \sim 10$ are similar in some respects to our results for bulk, cleaved $CrSi_2$ but there are also clear differences (loss of fine structure, greater overall width), as shown in Fig. 3. Since the only Cr silicide previously known to grow on Si upon reaction at 450 °C is $CrSi_2$, we conclude that either nonstoichiometric mixed phases or local bonding distortions are present at the Si–Cr interface.

The interpretation of the modification of the valence band with increasing coverage ($\theta < 10$) and of the early stages of interface formation is less clear cut than for Si–Ni. For Ni silicides the measured Ni 3*d* states were modified through changes in Ni–Ni interaction. The Si-rich Cr silicides are more complex; fewer Cr 3*d* states form the occupied nonbonding section of the *d* bands and these features lose importance compared to the deeper Cr–*d*/Si–*p* bonding states with increasing Si content. At the same time the overall width of this nonbonding section around E_F decreases but only the states below E_F are seen through photoemission and it is difficult to forecast the resulting experimental trend. Increasing the Cr content during interface formation ($\theta < 12$), however, we did not observe a change toward a lower density of states at E_F (similar to that of Cr_3Si) so that the modification of the valence band cannot be unambiguously related to a Cr–Si composition gradient as in the case of Si–Ni.

In this paper we have presented experimental results for several bulk Ni and Cr silicides and these have been compared to our calculations and to experimental results for the Si–metal interface. We have shown that the silicide density of states has a region of nonbonding character which falls between the hybridized Si–metal bonding and antibonding regions and that the nonbonding features are most visible in photoemission. By examining trends established experimentally and theoretically in the electronic properties of the Ni silicides, we have shown that the Si–Ni interface exhibits a concentration gradient starting from a NiSi-type situation during the early stages of formation and that there is no evidence of a $NiSi_4$-like phase or of interstitial Ni in silicon. The results for the Si–Cr interface are less clear cut and are being examined through systematics involving other refractory metal silicides.

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Bulk silicides and Si-metal interface reaction: Pd_2Si

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We report synchrotron-radiation photoemission studies of cleaved Pd_2Si in which we use 4*d* Cooper minimum and 4*p*—4*d* resonance techniques to identify the bonding Si *p*—Pd *d* states 3.5—6.5 eV below E_F, the Si *s* states at 9.3 eV, the nonbonding Pd 4*d* states centered at 2.5 eV, and hybridized Si-Pd or Pd *sp* states within 1.5 eV of E_F. The resonant photoemission technique was shown to yield detailed information about the orbital character of the valence states and to be applicable in principle to all Si—*d*-metal systems. Comparison of bulk Pd_2Si with palladium silicide thermally grown on Si(111) shows the main 4*d* emission feature at 2.8 eV shifted 0.3 eV to higher binding energy relative to bulk Pd_2Si, an increased full width at half maximum (2.5 versus 1.5 eV), and substantially greater emission from Si *p*—metal *d* bonding states. This confirms that the palladium silicide formed on Si is Si rich near the silicide-vacuum interface and shows that the electronic structure of the uppermost silicide layers differs from that of bulk Pd_2Si.

INTRODUCTION

The interface between two dissimilar materials frequently exhibits structural and electronic properties which are different from those of either material. These interfaces are of great fundamental and technological importance because of their role in Schottky barrier formation, proximity effects for superconductors, ohmic contacts, coherent modulated structures, etc. Major experimental and theoretical programs are presently underway which examine atomic diffusion, interface morphology, and electronic structures.[1–9]

To characterize the reactions which occur at interfaces requires a thorough understanding of Si-metal chemical bonding in bulk silicides. The electronic structure of Pd_2Si has been the subject of intense interest in connection with Si-Pd interface reaction.[6–8] However, all the data available so far concern silicides obtained by metal-film reaction on Si(111) following heat treatment that enhances surface segregation and causes composition gradients at the silicide-vacuum interface. The present study concerns bulk Pd_2Si samples cleaved *in situ* and represents the first systematic study of the *bulk* electronic structure of Pd_2Si, as emphasized by the relevant differences observed with respect to the previous literature.[6–8] To study the character of the electronic valence states, we systematically applied to Pd_2Si Cooper minimum and resonant-photoemission techniques. While both techniques have been previously applied to other systems for analyzing the electronic density of states, this is the first application to a bulk Si-metal compound. The present results clearly demonstrate the potential of such techniques in understanding the Si-metal chemical bonding and directly reflect on the modeling of the Si-Pd interface. Resonant photoemission obtains complementary information with respect to the Cooper minimum technique and allows investigation of the different contributions to the electronic density of states in the Si—3*d*-metal system where the other technique is not applicable.

EXPERIMENTAL

Bulk samples of Pd_2Si were prepared by co-melting high-purity palladium and silicon under an argon atmosphere in the water-cooled copper hearth of a nonconsumable arc furnace. The resulting buttons were zone refined to enhance grain growth. X-ray diffraction studies showed the $C22$ hexagonal (Fe_2P-type) structure of Pd_2Si with $a = 6.493 \pm 0.003$ Å and $c = 3.440 \pm 0.004$ Å.[10] Clean surfaces suitable for photoemission studies were obtained by fracturing the samples in the ultrahigh vacuum photoelectron spectrometer at operating pressures of $\sim 3 \times 10^{-11}$ Torr. Immediately after fracturing, the samples were positioned at the common focus of the monochromatic synchrotron-radiation beam and the

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[29]The intensities were normalized for monochromator output, storage ring beam current, etc., but assuming the transmission of the analyzer to be constant, i.e., the point-source approximation.

[30]The cross sections were measured after substracting a secondary background linearly interpolated between 10 eV and E_F. The use of different criteria does not modify the qualitative trend shown in Fig. 4.

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our bulk studies. The Si $2p_{1/2}$ core emission appears at 99.83±0.15 eV in this study and at 99.72 eV in Ref. 7 after heat treatment at 200 °C of Pd films evaporated on Si(100).

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Si–Cr AND Si–Pd INTERFACE REACTION AND BULK ELECTRONIC STRUCTURE OF Ti, V, Cr, Co, Ni, AND Pd SILICIDES

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We present a synchrotron radiation photoemission study of silicide nucleation at the Si(111)–Pd and Si(111)–Cr interfaces and of the electronic structure of bulk Pd_2Si, $CrSi_2$, $TiSi_2$, VSi_2, $CoSi_2$, $NiSi_2$ and Ni_2Si. These reveal the Si-p/metal-d hybridization, the bonding and nonbonding metal-derived d-features, and the decoupling of Si-p and Si-s states as predicted by recent calculations. Comparison of bulk silicides with Pd and Cr silicides thermally grown at the silicon–metal interface shows that the structure and composition of the first growth phases correspond to Pd_2Si and $CrSi_2$ but that the surface electronic structure exhibits an increase in the intensity of the bonding metal-d/silicon-p density of states features. Si-enrichment at the silicide–vacuum interface explains the apparent differences between the electronic structure of the interface and bulk silicides.

1. Introduction

Silicide growth at silicon–transition metal interfaces is of paramount importance in the technology of very large scale integrated circuits [1,2]. However, the microscopic mechanisms of Si–Si bond breaking and silicide formation are not sufficiently understood for detailed modeling of the interface chemistry. Indeed, it is only within the last few years that the flexible tools of the interface science (photoemission, LEED, Auger, TEM, RHEED, etc., and theoretical modeling) have been brought to bear on these important scientific and technological problems.

We have undertaken photoemission studies of bulk and interface silicides to examine the electronic interactions and growth properties of silicides. In this paper, we focus on the thermal processing of the Si–Pd and Si–Cr junctions and on the growth of the silicide phases at the interface (both Si–Pd [3–9] and the Si–Cr [10] have been extensively studied at room temperature). Results for the silicides grown on Si are compared to those for bulk Pd_2Si and $CrSi_2$ to

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SI-METAL INTERFACE REACTION AND BULK ELECTRONIC STRUCTURE OF SILICIDES

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We summarize synchrotron radiation photoemission results for cleaved, bulk 3d transition metal disilicides and for the interfaces of Si(111)-Cr, Si(111)-Ti, Si(111)-Ca, and Si(111)-Sm.

We have undertaken a series of synchrotron radiation photoemission studies which emphasize Si-metal interface formation and the electronic interactions in bulk metal silicides. The approach is twofold. First, we have performed step-by-step analysis of Si-Cr,[1] Si-Ti,[2] Si-Ca,[3] and Si-Sm[4] interface formation through analysis of the interface electronic structure as a function of metal coverage on cleaved Si(111). This work has included both room temperature and high temperature characterization of the silicides which grow on Si. The goal is to correlate the different reaction stages with the establishment of the junction parameters.[5] Second, we have conducted studies of the bulk silicides of Ti, V, Cr, Co, and Ni[6] to characterize Si-metal chemical bonding in general, to emphasize the effect of stoichiometry variations on the electronic structure, and for comparison of bulk silicides and interface reaction products.

In Fig. 1 we show photoemission spectra for several disilicides to provide a general picture of the electronic states of bulk 3d-metal disilicides.[7] As shown, the valence bands of the disilicides of Ti and V exhibit dominant 3d-derived spectral features 1-2 eV below E_F (full width at half maximum of 2.5-3 eV) and a relatively high density of states at E_F. These are primarily due to d states which are hybridized with Si p-derived states (shaded regions of DOS). As one moves across the 3d transition metal series, the primary feature shifts to higher binding energy and E_F falls in a region where an increasing number of non-bonding d states are present. The spectra for $CoSi_2$ and $NiSi_2$ show these predominantly non-bonding d states as a relatively narrow band (~3 eV below E_F for $NiSi_2$). The bonding d states appear as a shoulder at higher binding energy. Comparison of experiment with theory[8-9] reveals good agreement through the silicide series and demonstrates the importance of Si-p/metal-d hybridization for bonding.

While the nature of the chemical bond for transition metal silicides is becoming better established, almost nothing is known about bonding in metals which have few d electrons, notably the rare earths and the alkali metals.[5] In order to examine these systems and to contrast the interfacial and bulk electronic interactions of Si with d and non-d metals, we initiated studies of the Ca-Si and Sm-Si systems. Preliminary results for these interfaces show larger core level shifts than have been observed for the d-band metals (~1.5 eV for the Si 2p cores) and major reductions in the work function (more than 2 eV) during room temperature reaction. Furthermore, the Sm-Si system exhibits a Sm^{+2}-Sm^{+3} valence change that coincides with a transition between two stages of interface formation.

For these Si-Ca, Si-Sm, Si-Cr, and Si-Ti interfaces, the emission from intrinsic Si surface states is removed during the early stages of interface formation and the final value of the Schottky barrier is reached at submonolayer coverage. Room temperature studies show a subsequent second stage of interface formation when an extended, intermixed transition region between metal and semiconductor is formed. The intermixed phases exhibit electronic structures which differ from those of high temperature reacted interfaces.[4] The establishment of the Schottky barrier during the very early stages of interface formation and the relative independence of the barrier height on annealing treatment or silicide composition[2,10] suggest that the fundamental parameters of the junction are determined by microscopic reaction on a scale of 1-2 atomic layers rather than by the subsequent stages of Si-metal reaction.

The trends observed for Si-refractory metal, Si-rare earth, and Si-alkali earth interfaces, the absence of a sharp Si-metal boundaries, and the existence of complex interface morphologies adds substantially to the picture of Si interfaces which has previously included Cu, Ag, Au, Ni, Pd and Pt.[11] Further modeling of these systems will require systematic comparison of bulk and interface results and will include the inherent inhomogeneity of the Si-silicide-vacuum interface. Such studies are underway in several laboratories and major progress can be anticipated in the next few years.

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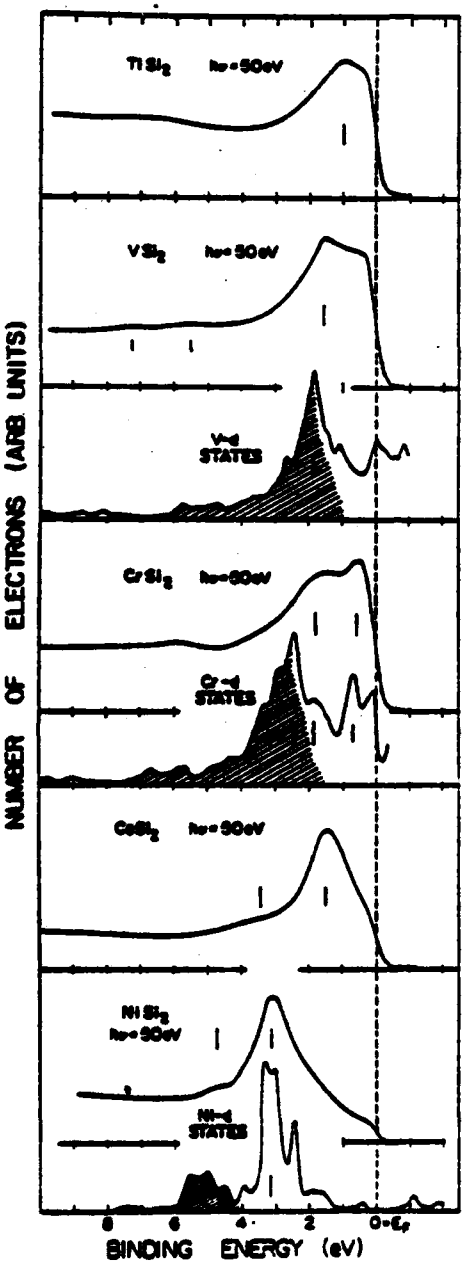

Fig. 1 Valence band emission and theoretical metal-d DOS (from Ref. 6) for 3d metal disilicides. Shading indicates Si-p/metal-d bonding states. For $TiSi_2$ and VSi_2, these hybrid d-p states are more readily seen than in $CoSi_2$ or $NiSi_2$ where the non-bonding d character dominates.

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Modulation of atomic interdiffusion at the Si(111)–Au interface

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We attained a wide modulation of the Si(111)–Au interface reaction by deposition of controlled amounts of Cr on the semiconductor surface before *in situ* junction fromation. Synchrotron radiation photoemission studies show that Cr deposition gives rise to a Si/Cr reacted interlayer that dramatically affects the subsequent Si–Au interdiffusion. Negligible interdiffusion of Cr and Au atoms was found in all cases so that the Si–Au intermixing depends upon an exchange reaction at the Si/Cr–Au interface in which Si is the only moving species. Large reduction of the interdiffusion occurs sharply above a critical value of Cr deposition (10 monolayers) that corresponds to a fully reacted Si(111)–Cr interface.

PACS numbers: 66.30.Ny

I. INTRODUCTION

Interdiffusion and chemical reactions at Si–metal interfaces is the subject of intense reserach aimed to explain the general properties of Si–metal junctions.[1–9] The problems range from estimating the influence of interface chemistry on the Schottky barrier height[10–14] to assessing the relative importance of thermal energy, extrinsic interface defects, and bulk Si–metal thermodynamics in determining the formation kinetics and the final structure of the junction.[1–9]

Recent experiments on compound semiconductors have drawn attention on the possibility of modulating interface reactions by varying the thickness of a thin simple metal interlayer deposited in the interface region between the semiconductor and a noble metal.[15,16] In what follows we present a study of the effect of a refractory metal (Cr) interlayer on the interface reaction between Si and Au. We attained a wide variation of the Si–Au reaction by modulating the interlayer thickness and we suggest that this effect is related to the varying local environment of the Si atoms in the Si/Cr interface phase. The different stages of interface reaction that we identified[17,18] during the formation of the Si(111)–Cr junction, therefore, are bound to correspond to a qualitatively different influence of the Cr interlayer on the Si–Au interdiffusion.[19] Such differences were examined through synchrotron radiation photoemission studies of the Si/Cr interface phase and of the overall Si/Cr–Au junction. Emission from the valence states and from the Si 2*p*, Cr 3*p*, and Au 4*f* core levels was examined as a function of the Cr coverage Θ_{Cr} on the silicon surface prior to Au deposition and as a function of Au deposition on Si/Cr phases of given composition. Cr coverage of 0.1–15 Å and Au coverage of 1–50 Å were examined and we will discuss here preliminary conclusions drawn mainly from valence band photoemission, focusing on the nature of the diffusion barrier effect of the Cr interlayer for $\Theta_{Cr} > 9$–10 Å. A quantitative presentation of the core results and a systematic analysis of the effect of the interlayer for $0.1 < \Theta_{Cr} < 15$ will be given in a following paper.[19]

II. EXPERIMENTAL

Interfaces were prepared *in situ* in an ultrahigh vacuum photoelectron spectrometer with operating pressure $\sim 3\times10^{-11}$ Torr (pressure was kept $< 4\times10^{-10}$ Torr during Cr sublimation and $< 1\times10^{-9}$ during Au evaporation). *N*-type, phosphorus-doped (1.5 Ω cm) Si single crystals oriented along the [111] direction were cleaved at precut notches to yield clean Si(111)-2×1 surfaces. Interlayers of given thickness were prepared by direct sublimation from a Ta boat or W basket onto the surface with coverage Θ_{Cr} monitored by a quartz thickness monitor. The consequent Si–Cr interface reaction gave rise to a Si/Cr intermixed phase[18,19] at the crystal surface. Such a phase was characterized by positioning the sample at the common focus of the monochromatic radiation beam and of the electron energy analyzer and recording photoelectron energy distribution curves (EDC's) of valence and core levels before and after Cr deposition. Studies of the Si–Au reaction were then carried out evaporating Au from a W coil. For clarity, we will define the Cr coverage as the "interlayer thickness" and both the Au coverage Θ_{Au} and Θ_{Cr} will be given in Å throughout the paper [in terms of the Si(111) surface atomic density of 7.6×10^{14} atoms/cm^2 it is 1 Å Cr = 1.1 monolayers, 1 Å Au = 0.8 monolayers].

Synchrotron radiation from the 240 MeV electron storage ring Tantalus at the University of Wisconsin–Madison was monochromatized with a 3 m toroidal grating monochromator ($12 < h\nu < 135$ eV), with a Seya–Namioka monochromator ($12 < h\nu < 30$ eV), or with a Grasshopper grazing incidence monochromator ($40 < h\nu < 140$ eV). The emitted photoelectrons were energy analyzed with a commercial double-pass cylindrical mirror analyzer with a typical overall resolution (electrons plus photons) of 0.3–0.4 eV. The data presented here represent numerous cleaves and repetitive measurements of the various stages of interface formation.

III. RESULTS: Si(111)–Cr AND Si(111)–Au

Any attempt at interpreting the present experimental data requires an *a priori* understanding of both the Si(111)–Au and the Si(111)–Cr interfaces. The Si(111)/Cr–Au system, in fact, was chosen primarily because both the Si–Cr and Si–Au interfaces are among the best characterized metal–semiconductor interfaces and because of its technological relevance.

For the Si(111)–Cr interface we have previously published an extensive synchrotron radiation photoemission investiga-

[illegible] in the previous paragraph, this parameter is related to the Si concentration in the Au film and in Fig. 1 is shown to be an acceptable parameter to gauge the Si–Au interface reaction. The resulting plot emphasizes the dramatic change in the Si–Au reaction that occurs for Θ_{Cr} [illegible] Å. The Cr interlayer effectively reduced the Si–Au interdiffusion only for interlayer thicknesses greater than 9 Å.

As we mentioned in Sec. III, the Si(111)–Cr interface is fully reacted at $\Theta_{Cr} = 9$ and further Cr depositions gives rise to the formation of an unreacted Cr film on top of the reacted

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SAMARIUM VALENCE CHANGES AND REACTIVE INTERDIFFUSION AT THE Si(111)-Sm INTERFACE*

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Synchrotron radiation photoemission studies show that the Si(111)2x1-Sm interface has a complex morphology involving sequential formation stages with different Sm valence states. For metal coverages up to 2-3 Å, Sm atoms appear only in a divalent state. At higher coverages (up to 10-15 Å) the trivalent Sm configuration dominates and large chemical shifts of Si 2p and Sm 4f and 5p levels are observed. The Sm valence change is related to the onset of the reactive interdiffusion of Sm and Si.

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Strongly bound chemisorption state for benzene on silicon (111)

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Dramatic differences were observed between the room-temperature reactivity of benzene on cleaved Si and on cleaved Ge and GaAs with synchrotron-radiation photoemission. No evidence of benzene adsorption was observed on Ge or GaAs. On Si we unexpectedly observed a strongly bound state, probably due to the formation of phenylic-like C–Si bonds.

PACS numbers: 68.45.Da, 82.65.My

Recent experiments[1] on pyridine molecules chemisorbed on Si and Ge surfaces detected stable chemisorption states due to the formation of chemical bonds involving nitrogen long-pair electrons. These results raised the following question: how can stable chemisorption bonds be formed between semiconductor surfaces and aromatic molecules without lone pairs? In particular, do stable chemisorption states exist at all for these systems? We tried to answer these questions by investigating the adsorption of benzene, the most fundamental aromatic molecule, on Si, Ge, and GaAs. Our synchrotron-radiation photoemission results show that no stable chemisorption state exists at room temperture for benzene on Ge and GaAs surfaces. Quite unexpectedly, however, we discovered a strongly bound chemisorption state for the benzene molecule on cleaved Si (111) at room temperature, presumably due to the removal of one H atom and the establishment of a C–Si bond.

These experiments were performed in an ultrahigh vacuum chamber with base pressure $<4\times10^{-11}$ Torr.[2] The samples were either cleaved in benzene atmosphere or cleaved in vacuum and then exposed to benzene vapors. The surfaces obtained with both procedures gave the same photoemission spectra. The benzene pressure was $0.6–3\times10^{-7}$ Torr, with purity tested by a mass spectrometer. At the end of each exposure the benzene was evacuated, thereby restoring the ultrahigh vacuum. The photoemission spectra were taken upon excitation by monochromatized 12–30-eV photons from the University of Wisconsin Storage Ring Tantalus, using a computer-controlled double-pass cylindrical mirror analyzer.

The dramatic differences between cleaved Si and GaAs surfaces exposed to benzene are emphasized by Figs. 1 and 2 where we show photoemission spectra for ~180 Langmuirs (L) of benzene of cleaved Si (111) 2×1, and for much higher exposures for cleaved GaAs (110). The spectra of Fig. 1 clearly exhibit the three most intense features of the gas-phase benzene photoemission spectra,[3] peaks, C, D, and E. In contrast, the spectra of Fig. 2 for GaAs, taken at exposures 1–2 orders of magnitude larger than for Si, exhibit only the spectral features of clean GaAs (110).[4] Similar experiments on benzene-exposed Ge (111) give only the spectral features of clean Ge (111) after exposures in the 600–1000-L range.

The results shown in Fig. 1 are representative of numerous cleaves of Si and were nearly insensitive to the quality of the cleave. Experiments using *s*-polarized light (with the po-

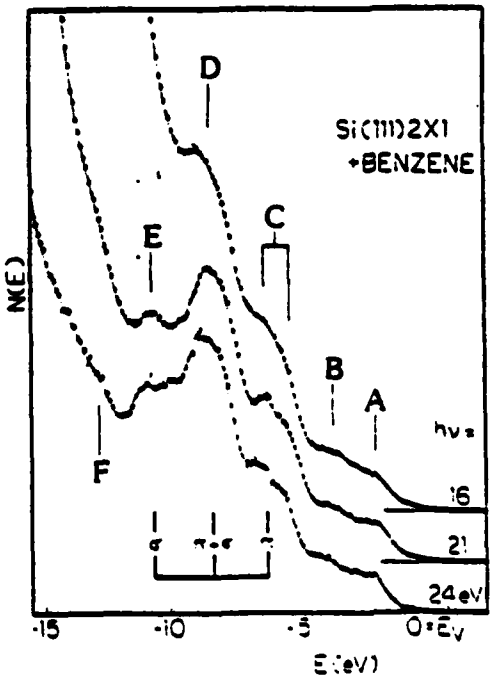

FIG. 1. Angle-integrated photoemission spectra taken on benzene-covered Si (111) 2×1 exposure ~180 L. The raw data are shown together with computer-generated smooth lines. The zero of the horizontal scale is the upper edge of the spectra, E_V. For comparison, vertical lines mark the positions of the three most intense spectral features of gas-phase benzene, with symmetry π, $\pi-\sigma$ and σ (see Ref. 3, these positions were aligned with respect to our spectra to obtain the best fit).

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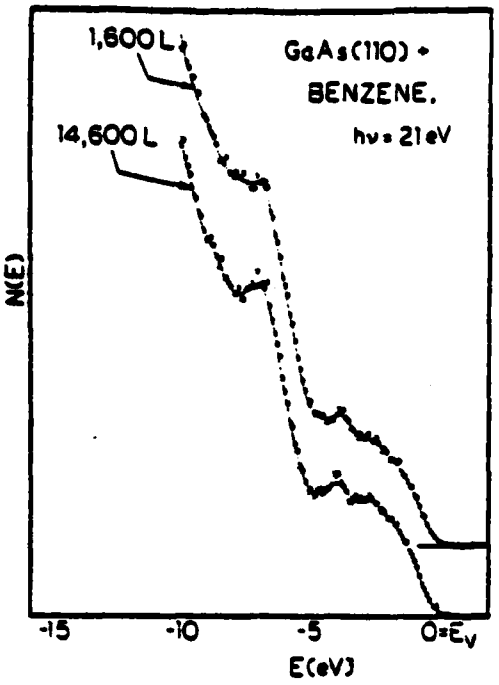

FIG. 2. Photoemission spectra taken on cleaved GaAs (110) after much larger benzene exposures than that of Fig. 1. Both spectra are close to the clean-GaAs spectra (see Ref. 3) and show no evidence of benzene adsorption.

larization vector perpendicular to the plane of incidence) and mixed *s*- and *p*-polarized light[2] produced spectra which exhibited little dependence on the polarization. Furthermore, the spectral line shape did not change with the benzene exposure, for total exposures in the range 1–180 L.

We observe in Fig. 1 six different features, labeled A–F. Of these, the marginally resolved doublet C and the peaks D and E correspond to the most intense $1e_{1g}(\pi)$, $1a_{2u}(\pi) + 3e_{2g}(\sigma)$ and $3e_{1u}(\sigma) + 1b_{2u}(\sigma) + 1b_{1u}(\sigma)$ bands of gas-phase benzene. The presence of those features shows that the benzene molecule is not decomposed although, as we shall discuss below, there are indications that one of its H atoms is replaced in the chemisorption bonding process. The weak feature F probably corresponds to the benzene $1e_{1g}(\sigma)$ band.[3] The remaining features, peaks A and B, are likely to be related to the formation of chemisorption bonds involving the "dangling bond" of the Si (111) surface. The experimental positions of peaks A, B, D, E, and F, measured from the upper edge of the spectra, E_v are -2, -3.7, -8.5, -10.8, and -12.8 eV (accuracy: ± 0.2 eV). The two components of peak C are 5.5 and 6.4 eV below E_v. No spectral features of clean Si were observed, consistent with previous studies of chemisorption of organic molecules.[1]

Two chemisorption configurations were examined to explain the above features. The first configuration is with the benzene ring parallel to the Si surface, and with chemisorption bonds involving the benzene π orbitals.[5] The second configuration is with the ring not parallel to the surface, and with formation of Si–C bonds upon removal of a H atom.[6] *A priori*, it would seem that the first configuration should be preferred because of the magnitude of the activation energy required to remove one of the H atoms. However, several facts indicate that the second configuration is the one occurring in this case. First, a geometry with the benzene ring parallel to the surface would imply strong photon-polarization effects in the spectral features related to benzene π orbitals—as it was observed, for example, for the σ bonds of Cl on Si (111).[7] However, these strong effects were not observed. Instead, the results are more consistent with the standing-up configuration, since this nonparallel configuration should give much weaker polarization effects due to the mixed p_z and p_{xy} character of the spectral features. Second, the two peaks A and B close to E_v appear related to the formation of bonds involving the Si atoms. Qualitatively similar structures are produced upon formation of Si–Cl and Si–H bonds,[7,8] although their positions in energy are different from those of peaks A and B. Finally, we observed a removal of the gas-phase degeneracy of peak C, similar to what is observed for all molecules derived from benzene upon substitution for a H atom by a different atom or radical.[3]

In conclusion, we found a unique, strongly bound chemisorption state for benzene on room-temperature Si (111), not observed for Ge or GaAs. Our experimental results suggest a chemisorption geometry with the benzene ring *not* parallel to the surface, and the formation of a chemisorption bond between Si and C, leading to a phenylic configuration. At the moment, the cause of the different reactivity of benzene on Si and on Ge and GaAs is not clear.

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AN INTERFACE CATALYTIC EFFECT: Cr AT THE Si(111)-Au INTERFACE

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ABSTRACT

Synchrotron radiation photoemission studies of the effect of Cr interlayers on Si(111)-Au interface reaction show that Cr concentrations below 1 x 10^{15} atoms/cm^2 retard Si-Au intermixing, concentrations between 1 and 7.5 x 10^{15} atoms/cm^2 promote Si-Au intermixing, and concentrations in excess of 8 x 10^{15} atoms/cm^2 sharply reduce intermixing. These variations are shown to depend on the three formation stages of the Si-Cr junction. Cr itself is shown only to be indirectly involved in the Si-Au reaction and Si is to be the only moving species.

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Stoichiometry and Structural Disorder Effects on the Electronic Structure of Ni and Pd Silicides

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ABSTRACT

Synchrotron radiation ultraviolet photoemission studies of the electronic structure of both stoichiometric epitaxial silicides ($NiSi_2$ and Pd_2Si) and metal rich phases (Ni_xSi and Pd_xSi) obtained by low energy ion sputtering (1KeV) are performed. The data for thick (1000-2000Å), annealed epitaxial stoichiometric silicides ($NiSi_2$ and Pd_2Si) are in good agreement with first principle and semiempirical calculations, indicating little variation of the surface electronic structure with respect to the bulk. The spectra associated with varying average metal concentrations ($x = 0.5$ to 3.5 for nickel silicides and $x = 2$ to 7.6 for palladium silicides) are dominated by the local atomic bonding configuration: for nickel silicides, the $NiSi_2$ structure is replaced by NiSi and Ni_2Si subunits in a discrete fashion as the average metal concentration increases while, for palladium silicides, the Pd_2Si local bonding remains dominant. A large number of Ni_xSi and Pd_xSi mixtures could be

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Electronic Structure of Cr Silicides and Si-Cr Interface Reactions

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Abstract

We present synchrotron radiation photoemission studies of bulk $CrSi_2$ and silicide phases grown on Si by thermal processing of the Si-Cr interface. Experiment shows that Si-Cr interface formation at room temperature results in reacted phases that differ from both bulk $CrSi_2$ and *in situ* grown Si-rich $CrSi_2$. Extended Huckel LCAO calculations of the density of states of Cr_3Si, CrSi, and $CrSi_2$ show that Si-Cr bond formation involves Si-p and Cr-d states with minimal charge transfer.

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41. We did not attempt a deconvolution of the spin-orbit components of the Si 2p and Cr 3P doublets. The quoted binding energies correspond to the peak intensities with respect to a linearly extrapolated secondary background.

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